

methy1, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches; a polyolefin, such as an ethylene homopolymer, that contains about 20 to about 150 branches per 1000 methylene groups, and that contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches; an ethylene homopolymer with a density of 0.86 g/ml or less; a homopolypropylene with a glass transition temperature of -30 °C or less, having at least 50 branches per 1000 methylene groups; a conventional high density polyethylene; and a low density polyethylene or linear low density polyethylene polymer.

REMARKS

Applicants acknowledge with appreciation the Examiner's observation that no prior art has been located that anticipates or renders obvious the subject matter of the claims of the present application. Applicants believe that in view of the present amendments the Examiner's objections to the specification are overcome. Applicants further submit that the claims are in condition for allowance and offer the following remarks in support of said submission.

The Examiner stated that the Information Disclosure Statement filed on June 22, 2001 fails to comply with 37 C.F.R. §1.98(a)(3) because it does not include a concise explanation of the relevance of each patent listed that is not in the English language. Applicants believe that the Examiner is apparently referring in particular to the article "Studium vetveni polyethyleny nuklearní magnetickou rezonancní spektroskopii", Jan Tecl, Chemický Průmysl roc. 37/62, pp. 196-200 (1987). Applicants do not have an English translation of the document, and relied upon it with regard to its disclosure of NMR spectra. Applicants provide a statement of the relevance of this document in the Supplemental Information Disclosure Statement filed herewith. Applicants request that the Examiner consider the document and indicate that he has done so by initialing the

enclosed form PTO/SB/08B and returning a copy of the initialed form to Applicants' attorney.

The Examiner has objected to the specification on several bases. With regard to the Examiner's objection to the reference on page 131, lines 37-37, to claims that were in the application as originally filed, Applicants have amended the specification to recite the subject matter that was in original claims 1, 3, 4, 6, 332 and 343. This amendment introduces no new matter and is supported in the application as originally filed, *inter alia*, in claims 1, 3, 4, 6, 332 and 343.

In response to the examiner's objection to pages 274 and 277, clean copies of pages 274 and 277 are provided herewith.

In response to the Examiner's objections to the notation on page 383 adjacent to the table entitled "¹³C NMR data", new pages 382-383 are provided herewith. Page 382 has been amended to include under Example 458 the NMR data relied upon in the quantitative analysis of the polypropylene prepared in Example 458. This amendment introduces no new matter, and merely presents the data in its proper location in connection with the experimental procedure for which the data was obtained.

Rejections under 35 U.S.C. § 112

Claims 563-574 were rejected under 35 U.S.C. § 112. The Examiner stated that the specification does not "reasonably provide enablement for any and all catalyst formulations". This rejection is respectfully traversed. Applicants respectfully submit that claims 563-574 are not drawn to "any and all catalyst formulations", but to "transition metal containing coordination polymerization catalysts". The claims further recite that the claimed process is carried out under certain polymerization conditions, specifically conditions that produce in the polymers an amount of branching that is outside the predicted number of branches. Moreover, adequate guidance is provided in the specification for one skilled in the art to ascertain what modifications might be made to polymerization conditions to obtain the desired amount of branching in a polymer. For example, on page 90 beginning on line 15, the effects of pressure and temperature on the degree of branching are disclosed. Although Applicants have observed the surprising and

unexpected result that the amount of branching obtained in polymers formed according to the processes disclosed in the present application differs from that predicted by the equation on page 100, Applicants submit that one skilled in the art, armed with Applicants' disclosure, could adapt the polymerization conditions in order to produce a desired amount of branching. Applicants further submit that the selection of an appropriate transition metal catalyst for use in making a particular polymer with a desired degree of branching would not require undue experimentation by one skilled in the art.

Applicants respectfully direct the Examiner's attention to the Examples, which demonstrate the processes of the present invention with respect to catalysts containing other transition metals besides nickel and palladium. Examples 430-438 illustrate the effects of various parameters on the amount of branching obtained when catalysts containing cobalt are used for polymerization according to the processes of the present invention. In Example 430, a catalyst based on CoI_2 was used to polymerize ethylene at a pressure of 140 kPa at room temperature, and the resulting polymer had 100 methyl groups per methylene. In Example 432, under the same conditions, polymerization using $[(2,6\text{-}i\text{PrPh})_2\text{DABMe}_2]\text{CoMe}_2$ yielded polyethylene having 115 methyl per methylene. Example 433 shows that, using the same catalyst, polymerization under an ethylene atmosphere of only 6.9 Mpa at lower temperatures produced a polyethylene having 18 methyl per methylene. The breadth of the scope of these examples provides support for the processes recited in claims 563-574, and the specification provides adequate teaching for one skilled in the art to carry out the claimed processes. The fact that the degree of branching that can be obtained is different from what would be predicted is merely indicative of the surprising and unobvious results obtained by Applicants and recognized by the Examiner. Accordingly, Applicants respectfully submit that the claims meet the requirements of 35 U.S.C. § 112, first paragraph.

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CONCLUSION

Applicants believe claims 563-574 to be in condition for allowance. Withdrawal of all rejections of record and prompt allowance of all of the claims is therefore respectfully requested.

Respectfully Submitted,

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By: Gail Dalickas
Gail A. Dalickas
Reg. No.: 40,979
Telephone: (302) 984-6282
Facsimile: (302) 658-1192

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

(b) at least one other natural or synthetic polymer chosen from [the polymer of claims 1, 3, 4, 6, 332, or 343,] the following: a polyolefin, such as an ethylene homopolymer, that contains about 80 to about 150 branches per 1000 methylene groups, and that contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches; a polyolefin, such as an ethylene homopolymer, that contains about 20 to about 150 branches per 1000 methylene groups, and that contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, about 1 to about 12 propyl branches, about 1 to about 12 butyl branches, about 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches; an ethylene homopolymer with a density of 0.86 g/ml or less; a homopolypropylene with a glass transition temperature of -30 °C or less, having at least 50 branches per 1000 methylene groups; a conventional high density polyethylene[.]; and a low density polyethylene or linear low density polyethylene polymer.

Example 231

B²

A Schlenk flask containing 73.2 mg (0.0500 mmol) of $\{[(2,6\text{-i-PrPh})_2\text{DABMe}_2]\text{PdMe}(\text{OEt}_2)\}^+\text{BAF}^-$ was evacuated, cooled to $-78\text{ }^\circ\text{C}$, and then back-filled with ethylene (1 atm). Chlorobenzene (50 mL) was added via syringe and the solution was allowed to warm to room temperature. After 0.5 h, the reaction vessel was very warm and ethylene was being rapidly consumed. The reaction flask was then placed in a room-temperature water bath and stirring was continued for a total of 3 h. A very viscous solution formed. The atmosphere was then switched to ethylene/carbon monoxide (1:1 mixture, 1 atm) and the reaction mixture was stirred for 47.7 more hours. During this time, the solution became slightly more viscous. The polymer was then precipitated by adding the chlorobenzene solution to methanol. The methanol was decanted off of the polymer, which was then partially dissolved in a mixture of Et_2O , CH_2Cl_2 and THF. The insoluble polymer fraction (2.71 g) was collected on a sintered glass frit, washed with chloroform, and then dried in a vacuum oven at $70\text{ }^\circ\text{C}$ for 12 h. The NMR spectroscopic data of the gray rubbery material are consistent with the formation of a diblock of branched polyethylene and linear poly(ethylene-carbon monoxide): ^1H NMR (CDCl_3 /pentafluorophenol, 400 MHz) δ 2.85 ($-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})-$), 2.77 ($-\text{C}(\text{O})\text{CH}_2$, minor), 1.24 (CH_2), 0.83 (CH_3); Polyethylene Block Branching: $\sim 103\text{ CH}_3$ per 1000 CH_2 ; Relative Block Length $[(\text{CH}_2\text{CH}_2)_n-\text{C}(\text{O})\text{CH}_2\text{CH}_2)_m]$: $n/m = 2.0$. ^{13}C NMR (CDCl_3 /pentafluorophenol, 100 MHz; data for ethylene-CO block) δ 211.6 ($-\text{C}(\text{O})-$), 211.5 ($-\text{C}(\text{O})-$, minor), 35.9 ($\text{C}(\text{O})-\text{CH}_2\text{CH}_2-\text{C}(\text{O})$), 35.8 ($\text{C}(\text{O})\text{CH}_2$, minor).

Example 235

Synthesis of an ethylene polymerization catalyst
from Ni(MeOCH₂CH₂OMe)Br₂ and MeC(=N-2,6-C₆H₃-
iPr₂)CH=C(NH-2,6-C₆H₃-iPr₂)Me

5 Ni(MeOCH₂CH₂OMe)Br₂ (0.110 g, 0.356 mmol) and
MeC(=N-2,6-C₆H₃-iPr₂)CH=C(NH-C₆H₃-iPr₂)Me (0.150 g,
0.359 mmol) were combined in 10 mL of methylene
chloride to give a peach-colored suspension. The
reaction mixture was stirred at room temperature
10 overnight, during which time a lavender-colored powder
precipitated. This was isolated by filtration, washed
with petroleum ether and dried affording 0.173 g of
material. This compound was used as the catalyst in
Example 233.

Example 236

B3
15 {[(2,6-i-PrPh)₂DABMe₂]Pd(MeCN)₂}(BF₄)₂
[Pd(MeCN)₄](BF₄)₂ (0.423 g, 0.952 mmol) and (2,6-
i-PrPh)₂DABMe₂ (0.385 g, 0.951 mmol) were dissolved in
30 mL acetonitrile under nitrogen to give an orange
20 solution. The reaction mixture was stirred at room
temperature overnight; it was then concentrated in
vacuo to afford a yellow powder. Recrystallization
from methylene chloride/petroleum ether at -40°C
afforded 0.63 g of the title compound as a yellow
25 crystalline solid. ¹H NMR (CD₂Cl₂) δ 7.51 (t, 2H,
H_{para}), 7.34 (d, 4H, H_{meta}), 3.22 (sept, 4H, CHMe₂),
2.52 (s, 6H, N=CMe), 1.95 (s, 6H, NC≡Me), 1.49 (d, 12H,
CHMe₂), 1.31 (d, 12H, CHMe₂).

Example 237

30 Ethylene Polymerization Catalyzed by {[(2,6-i-
PrPh)₂DABMe₂]Pd(MeCN)₂}(BF₄)₂

A 100 mL autoclave was charged with a solution of
{[(2,6-i-PrPh)₂DABMe₂]Pd(MeCN)₂}(BF₄)₂ (0.043 g, 0.056
mmol) dissolved in 50 mL chloroform and ethylene (2.8
35 MPa). The reaction mixture was stirred under 2.8 MPa
ethylene for 9 h 15 min. During this time, the
temperature inside the reactor increased from 23 to
27°C. The ethylene pressure was then vented and

Polymerization was initiated by addition of methylaluminoxane (MAO; 1.5 mL 10% soln in toluene) and a propylene atmosphere was maintained throughout the course of the reaction. The reaction mixture was stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected, washed with water and acetone, and dried under vacuum. Yield = 1.41 g. DSC: T_g -53.6°C , T_m -20.4°C (apparent T_m is a small shoulder on the T_g). Quantitative ^{13}C NMR analysis, branching per 1000 CH_2 : Total methyls (226), \geq Butyl and end of chains (8.5), $\text{CHCH}_2\text{CH}(\text{CH}_3)_2$ (2.3), $-(\text{CH}_2)_n\text{CH}(\text{CH}_3)_2$ $n \geq 2$ (12.1). Based on the total methyls, the fraction of 1,3-enchainment is 53%. Analysis of backbone carbons (per 1000 CH_2): δ^+ (254), δ^+/γ (1.96).

Listed below are the ^{13}C NMR data upon which the above analysis is based.

^{13}C NMR data

Freq ppm	Intensity	
46.3126	6.77995	
46.079	6.56802	
45.463	7.82411	
45.2453	6.98049	
39.1764	8.95757	
38.4384	5.42739	
38.1145	20.5702	
37.8755	18.8654	
37.626	19.2917	
37.2702	128.202	
35.0773	6.30042	
34.5304	19.5098	
34.2543	38.6071	
33.7818	4.3205	
33.2986	16.3395	
32.9588	72.1002	
31.934	10.626	
31.419	5.57124	
30.5907	41.727	
30.1287	134.312	γ
29.7518	351.463	δ^+
29.3217	9.58971	
28.1589	21.1043	
27.9677	17.7659	
27.5589	44.1485	
27.3783	25.0491	
27.1766	119.562	
27.0226	52.4586	

~25.6		terminal methine of XXVIII
24.5908	8.69462	
24.4315	9.27804	
22.5253	30.7474	region of methyls of XXVIII and XXIX, 2B ₄ +, 2EOC
20.4333	20.0121	1B ₁
19.7271	103.079	1B ₁
14.7679	5.0022	
14.4068	4.56246	
13.8812	12.3077	1B ₄ +, 1EOC

Example 459

B⁵
Preparation of highly chain-straightened polypropylene with a low T_g. The complex [(2,5-*t*-BuPh)₂DABAN]NiBr₂ (0.0155g, 2.0x10⁻⁵ mol) was placed into a flame-dried 250 mL Schlenk flask which was then evacuated and back-filled with propylene. Freshly distilled toluene (100 mL) was added via syringe and the resulting solution was stirred in a water bath at room temperature. Polymerization was initiated by addition of 1.5 mL of a 10% MAO solution in toluene, and a propylene atmosphere was maintained throughout the course of the reaction. The reaction mixture was stirred for two hours at constant temperature followed by quenching with 6M HCl. Polymer was precipitated from the resulting solution with acetone, collected, washed with water and acetone, and dried under vacuum. Yield = 0.75 g. DSC: T_g -53.0°C, T_m none observed. Quantitative ¹³C NMR analysis, branching per 1000 CH₂: Total methyls (307), ≥ Butyl and end of chains (11.2), -CHCH₂CH(CH₃)₂ (11.5), -(CH₂)_nCH(CH₃)₂, n≥2 (5.9). Based on the total methyls, the fraction of 1,3-enchainment is 43%.

Example 460

Preparation of highly chain-straightened poly-1-hexene with a high T_m. A flame-dried 250 mL Schlenk flask under a nitrogen atmosphere was charged with 40 mL of freshly distilled toluene, 0.0133 g of [(2-*t*-BuPh)₂DABAN]NiBr₂ (2.0x10⁻⁵ mol), 5.0 mL of 1-hexene, and 55 mL more toluene (100 mL total volume of liquid).